

# Preparation and properties of novel sulfonated poly(phthalazinone ether ketone) based PEM for PEM fuel cell application

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## Abstract

Novel sulfonated poly(phthalazinone ether ketone) (SPPEK) was synthesized by direct polymerization via N–C coupling reaction. The membrane based on SPPEK was simply obtained by casting from 5% solution of SPPEK in *N,N*-dimethylacetamide (DMAc) at 60 °C. The as-made membrane was characterized by ion-exchange capacity (IEC), thermal analysis, proton conductivity, single cell performance and electrochemical impedance spectra (EIS). The SPPEK membrane showed excellent characteristic as a proton exchange membrane (PEM) for PEMFC application, such as high ionic exchange content (IEC) of 2.04 mequiv g<sup>-1</sup>, high water uptake of 50.6% at 100 °C, the proton conductivity of 1.06 × 10<sup>-2</sup> S cm<sup>-1</sup> at 20 °C, as well as the superior anti-hydrolytic ability and mechanical strength. Moreover, the membrane exhibited higher thermal stability than Nafion 115. Cell evaluation experiment demonstrated a better performance of SPPEK than that of Nafion 115-cell. Finally, electrochemical impedance spectra (EIS) was conducted to measure the charge transfer resistance to compare the difference between SPEEK and Nafion 115.

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**Keywords:** Fuel cell; Polyaromatics; PEM; MEA; PEMFC; Cell performance

## 1. Introduction

Proton exchange membrane fuel cells (PEMFC) are promising automotive, stationary, and portable power sources in view point of their low weight, high efficiency and the absence of noxious emissions [1,2]. A key issue for the commercial application of PEMFC is to develop the proton exchange membrane that should be inexpensive and massive production acceptable together with equivalent performance with Nafion. The Perfluorinated Nafion proton conductive membranes are commercially available today and are the most commonly used in PEMFC presently owing to their excellent performances and long term stability at moderate temperature, nevertheless, their application is greatly limited by their high cost, poor performance at temperature above 80 °C due to conductivity loss because of dehydration and high methanol permeability [3–5].

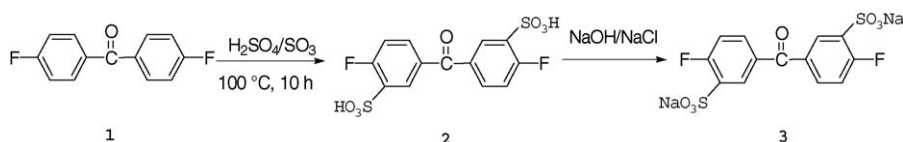
Poly(arylene ether)s including poly(aryl ether ketones), poly(aryl ether sulfone), and poly(phthalazinones) are high per-

formance engineering thermoplastic polymers. They have been extensively studied as cheaper alternatives for the commercial perfluorinated membranes by introduction of functional groups such as carboxylic acid [6], phosphonic acid [7] and sulfonic acid groups [8] onto the backbone or to the pendent side chains [9,10], which may also escape from other disadvantages of the perfluorinated membranes [11–16].

Among the polyaromatics mentioned above, sulfonated poly(phthalazinone ether ketone) (SPPEK) has been reported in previous work as a new kind of polymer with superior performance such as excellent chemical and oxidative resistance, mechanical strength, high thermal stability, glass transition temperature and proton conductivity [11,14–17]. SPPEK can be prepared by both the post-sulfonation of PPEK and the direct polymerization of pre-sulfonated monomers. The post-sulfonation may not only deteriorate the mechanical and thermal stabilities of resulting membrane material because of the cleavage of ether bond, but also fail to control the degree and location of sulfonation. However, these shortcomings can be partially overcome by the direct synthesis from sulfonated monomer [18–21]. More recently, a new SPPEK with excellent membrane properties was directly synthesized from sulfonated monomer

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Scheme 1. Synthesis of sulfonated 4,4'-difluorobenzophenone (SDFBP) **3**.

in our lab. With the special designed sulfonic groups adjacent to the N–C heterocyclic bond, the polymers showed better thermal and oxidative stability, reasonable water affinity and high proton conductivity. These characteristics are critical for the application as PEM in PEMFC. In this work, the larger scale synthesis of the SPPEK was carried out and very high-molecular weight (inherent viscosity being  $1.02 \text{ dL g}^{-1}$ ) was afforded. The membrane was cast from the dilute solution of the synthesized polymer. The as-made membrane was fully examined and subjected to the further evaluation of the application as PEM in PEMFC.

## 2. Experimental

### 2.1. Preparation of proton exchange membrane (PEM)

According to the procedure described by Wang et al. [22], difluorobenzophenone (DFBP) **1** was treated in fuming sulfuric acid (50%), then neutralized first by sodium chloride and subsequently by sodium hydroxide at room temperature to give sulfonated 4,4'-difluorobenzophenone (SDFBP) **3**, as depicted in Scheme 1.

Dicarboxylic acid **6** containing biphenyl moiety was synthesized by the polymerization of 2-(4-chlorophenyl)benzoic acid **4** with 4,4'-dihydrodiphenyl **5** in the presence of anhydrous  $\text{K}_2\text{CO}_3$  in DMAc and toluene. The resulting **4** was cyclized

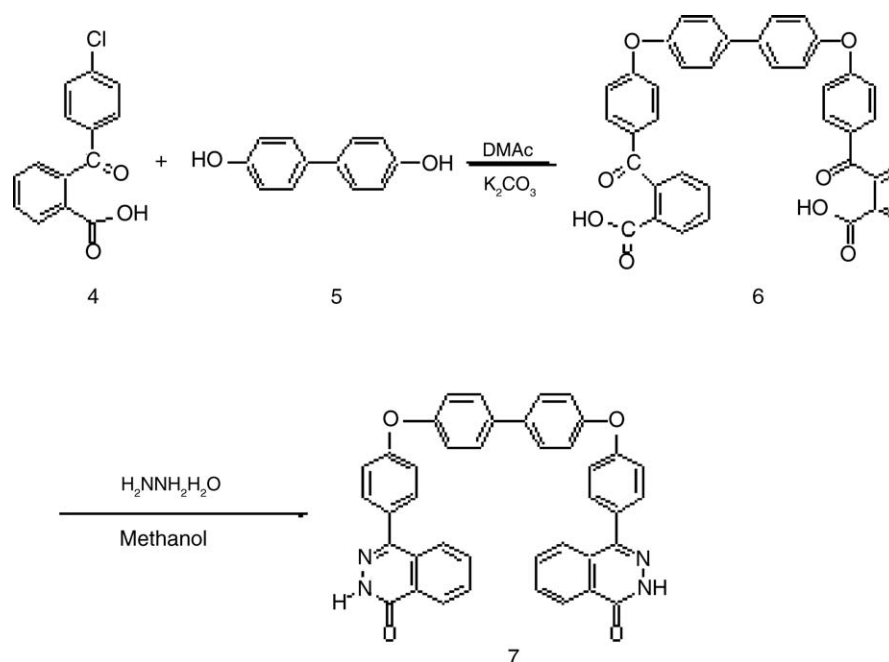
using hydrazine monohydrate in methanol to give bisphthalazinone monomer **7**, as depicted in Scheme 2. [23] Finally, the bisphthalazinone monomer **7** reacted with SDFBP **3** to give high-molecular-weight sulfonated poly(phthalazinone ether ketone) (SPPEK) **8**, as depicted in Scheme 3.

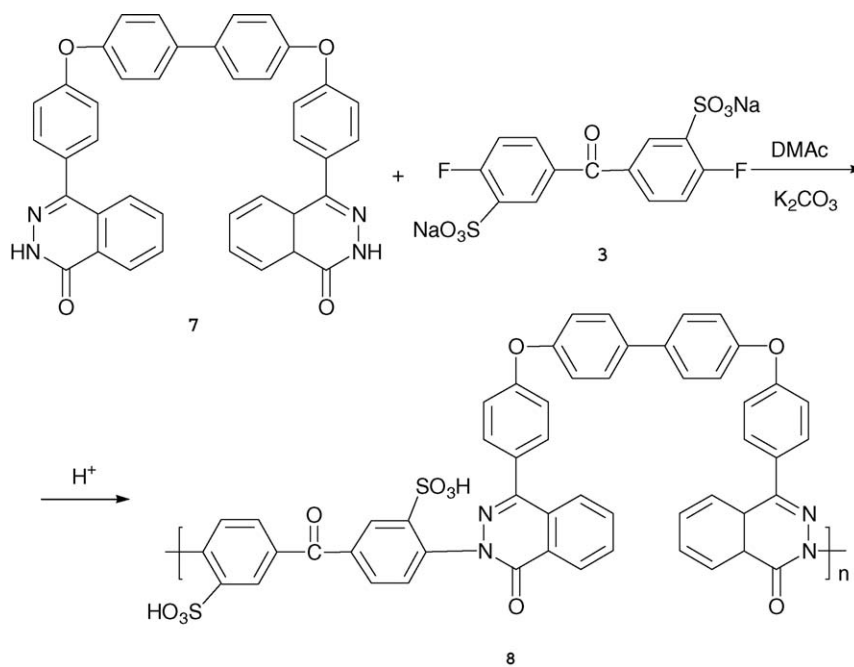
The PEM of SPPEK was prepared by casting from a 5% SPPEK solution in DMAc on a glass plate in a dust-free environment and dried at  $60^\circ\text{C}$  for 12 h and then at  $110^\circ\text{C}$  under vacuum for 48 h.

### 2.2. MEA preparation

TGP-H-120 carbon paper (Toray) with the thickness of  $330 \mu\text{m}$  was used for gas diffusion media (GDM). The received carbon papers were cut out and washed in acetone and alcohol in order to remove dust and grease materials, followed by dipping entirely into a 20 wt.% PTFE solution for 1 min. Thereafter, the carbon papers were dried again at the room temperature for 1 h, and were subjected to heat-treatment in the oven for 30 min at 110, 280 and  $350^\circ\text{C}$ , respectively. The heat-treatment at different temperatures can enhance the homogeneity of the PTFE film. The as-treated carbon papers were used as gas diffusion layer (GDL).

The 20 wt.% Pt/C (E-TEK) was used as an electrocatalyst on both the cathode and anode. The electrocatalyst slurry in 5 wt.% Nafion solution was prepared to provide a more intimate contact between the polymer electrolyte membrane and platinum par-

Scheme 2. Synthesis of bisphthalazinone monomer **7**.



Scheme 3. Synthesis of sulfonated poly(phthalazinone ether ketone) 8.

ticles. The weight ratio of supported Pt catalyst to pure Nafion was maintained at 3:1 and the ratio of Pt catalyst to iso-propanol at 3:5. The slurry was mixed thoroughly using a magnetic stirrer for 3 h and then ultrasonicated for another 1 h. The catalyst slurry was coated onto one side of the GDL by simply brushing and acted as catalyst layer after drying at 80 °C for 1 h in the vacuum oven. The GDL with catalyst layer was prepared by hot-pressed on double sides of pre-treated Nafion 115 membrane or the membranes synthesized in our lab for 60 s at 120 °C under a pressure of 60 atm to yield a membrane electrode assembly (MEA) [24].

### 2.3. Measurement

#### 2.3.1. Membrane

The water swelling experiments were conducted by measuring the weight and the length differences between fully hydrated membrane and dried membrane. The membranes were first vacuum dried at 80 °C for 24 h and then weighed. They were equilibrated in water at 30, 50, 80, 100 °C for 24 h, respectively, and quickly dry-wiped, weighed and measured. The linear expansion rate ( $L\%$ ) and water absorption ( $W\%$ ) were obtained via the following Eqs. (1) and (2):

$$L (\%) = (L_1 - L_0) \times \frac{100}{L_0} \quad (1)$$

$$W (\%) = (W_1 - W_0) \times \frac{100}{W_0} \quad (2)$$

where  $L_0$  and  $L_1$  are the length of membranes before and after water absorption, respectively;  $W_0$  and  $W_1$  are the mass of membranes before and after water absorption, respectively.

Thermal stabilities of the polymers was determined with Seiko SSC-5200 thermogravimetric analyzer [thermogravimet-

ric analysis (TGA)/differential thermal analysis (DTA)] under a protective nitrogen atmosphere (200 mL min<sup>-1</sup>) at the heating rate of 20 min<sup>-1</sup>. The glass-transition temperature ( $T_g$ 's) was determined on a Seiko 220 DSC instrument at a heating rate of 20 °C min<sup>-1</sup> under nitrogen protection.

Proton conductivity measurement was performed on fully hydrated membranes using Solartron electrochemical interface 1287 and 1255B instrument functioning with an oscillating voltage of 10 mV using two probes with the frequency between 1 MHz and 5 kHz.

#### 2.3.2. PEMFC

A single PEMFC using the aforesaid MEA inside was operated at a cell temperature of 50 °C with pure hydrogen and oxygen as reactant gases, which were fed into the cell at 68 mL min<sup>-1</sup> and were externally humidified by bubbling through a water bath of 70 °C at the pressure of 0.20 MPa.

The EIS measurements were carried out online when PEMFC was working. The amplitude of the AC signal was 10 mV and the frequency was varied from 50 mHz to 100 kHz. The anode at hydrogen side was used as the reference and the counter electrode; the cathode at oxygen side was acted as the working electrode.

## 3. Results and discussion

### 3.1. Physical–chemical characteristics of SPPEK membrane

The physical–chemical characteristics of SPPEK membrane are shown in Table 1, and the properties of Nafion 115 are also included for comparison.

Table 1  
Physical–chemical characteristics of membranes

	EW (g mequiv. <sup>-1</sup> )	IEC by titration (mequiv. g <sup>-1</sup> )	Proton conductivity ( $\times 10^{-2}$ S cm <sup>-1</sup> )	Thickness ( $\mu\text{m}$ )
SPPEK	490	2.04	1.06	80
Nafion 115	1100	0.91	2.03	125

Both high proton conductivity and reasonable mechanical strength are essential properties for electrolyte membrane. Above properties are generally affected by the IEC value greatly. Usually proton conductivity increases with increasing IEC value, whereas mechanical strength decreases with this increase. Fortunately, the as-made SPPEK membrane with a IEC value of 2.04 mequiv. g<sup>-1</sup> seemed to show little change in its appearance and strength subjecting to immersion in 100 °C water for about 100 h. This indicated that the anti-hydrolytic ability and mechanical strength of the SPPEK membrane is available for the application in PEMFC as a PEM. The two properties are much better than those of other sulfonated polymers reported in the literature [25–27]. Due to the high IEC value, the SPPEK membrane had high proton conductivity of  $1.06 \times 10^{-2}$  S cm<sup>-1</sup> at 20 °C, which was very close to that of Nafion 115. Moreover, the thickness of the SPPEK membrane can be readily tailored by changing the casting concentration of SPPEK solution. In this regard, the membrane with a smaller thickness of 80  $\mu\text{m}$  could exhibit equivalent proton conductivity when compared to the Nafion 115 with a thickness of 125  $\mu\text{m}$ . As shown in Table 1, SPPEK had higher IEC value but had lower proton conductivity compared with Nafion 115. This is due to that Nafion 115 with the sulfonic acid groups on the perfluorinated chain is activated easily by the electron withdrawing F atoms, resulting in a stronger acidity.

### 3.2. Water swelling

Table 2 shows the effect of the temperature of hydrothermal treatment on the swelling ratio and water absorption of SPPEK and Nafion 115, respectively. Appropriate hydration of the membrane is critical for fuel cell application due to its profound effect on proton conductivity and mechanical property. Water assists

Table 2  
Swelling ratio and water uptake of membranes at different temperature

	Water temperature, 24 h			
	30 °C	50 °C	80 °C	100 °C
<b>SPEEK</b>				
Swelling ratio (%)				
Length	31.6	36.3	41.6	49.6
Width	7.1	7.1	12.9	14.7
Water uptake (%)	22.8	30.9	46	50.6
<b>Nafion 115</b>				
Swelling ratio (%)				
Length	8.9	13.9	19	21.1
Width	5.7	7.5	8.8	9.8
Water uptake (%)	15.0	19.0	24.9	26.8

the transportation of protons from the anode to the cathode. If the electrolyte membrane is insufficient hydrated, its conductivity falls dramatically. On the other hand, water excess results in electrode flooding and morphological instability of the membrane. The water sorption and swelling ratio increase with increasing sulfonation content owing to the strong hydrophilicity of sulfonic acid groups, to some degree, the polymeric membrane deteriorates because of its dissolution in hot water. The water uptake and swelling ratio of SPPEK and Nafion 115 as a variable of temperature are listed in Table 2. It can be seen that the swelling ratio and water uptake of both membranes increased with the water temperature up to 100 °C. Moreover, SPPEK membrane showed greater swelling ratio and water absorption than Nafion 115 membrane at the same temperature due to higher content of hydrophilic sulfonic acid groups (higher IEC value) in the SPPEK molecule. In spite of the greater swelling ratio and water absorption, good mechanical strength of SPEEK membrane at 100 °C from the observation of mechanical strength experiment can ensure its potential application as PEM in the fuel cell. It can also be seen from Table 2 that the swelling ratios of length (*x*-direction) to width (*y*-direction) of the as-made SPPEK membrane were larger than those for Nafion 115. This behavior was resulted from the anisotropy of the membranes that is not favor the practical application of the membrane in the fuel cells.

### 3.3. Thermal stability

Thermal stabilities of SPPEK and Nafion 115 were determined by TGA and DSC as shown in Fig. 1. For SPPEK, a two-step degradation profile was evidenced. The first weight loss (about 20 wt.%) at about 300 °C was attributed to the elimination

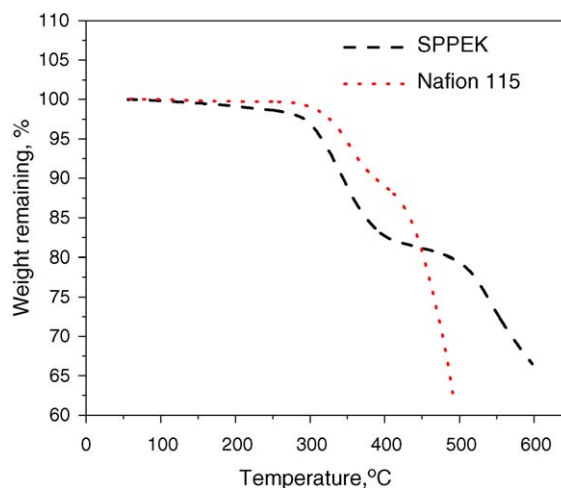


Fig. 1. TGA trace of sulfonated poly(phthalazinone ether ketone).

of sulfonic acid groups and the small amount of absorbed water, whereas the second weight loss peak at about 450 °C was due to the degradation of the main chain of SPPEK. To minimize the effect of the absorbed water, the measurements were performed following the way that the samples were heated to 150 °C to get rid of absorbed water in nitrogen flow, cooled down to 80 °C and finally the heating history from 80 to 600 °C was recorded. DSC measurement of the synthesized polymer at temperatures ranging from 30 to 300 °C did not show glass transition temperature ( $T_g$ ) before thermal decomposition. The highly thermal stability and the absence of glass temperature below 250 °C were resulted from both the rigid nature and the ionomer characteristic of SPPEK molecule, which show the promising PEM as an application in high temperature PEMFC.

### 3.4. Cell evaluation

The polarization curves of single H<sub>2</sub>/O<sub>2</sub> fuel cell using the MEAs based on SPPEK and Nafion 115 membranes were shown in Fig. 2. It can be seen that SPPEK-cell showed better electrochemical performance than Nafion 115-cell in the whole current density range. Obviously, SPPEK-cell had much higher open circuit voltage (OCV) than Nafion 115-cell. The open circuit voltage (OCV) is a good measurement of H<sub>2</sub> or O<sub>2</sub> crossover through the PEMs to the cathode or anode [28], therefore, SPPEK had stronger ability to suppress the gas crossover (lower gas permeation) when compared with Nafion 115. At the potential of 0.6 V, the current density of SPPEK-cell and Nafion 115-cell reached 0.6 and 0.5 A cm<sup>-2</sup>, respectively. The voltage collapse of Nafion 115-cell appeared at the current density of 0.67 A cm<sup>-2</sup>, whereas that of SPPEK-cell was inconspicuous even at 0.74 A cm<sup>-2</sup>. It appeared to be contradictory that SPPEK with lower proton conductivity showed better electrochemical performance than Nafion 115. In fact, the deterioration in electrochemical performance is an indicative of local water depletion in the membrane due to the electro-osmotic drag of water from the anode to the cathode [29]. The drying out on the anode side is more pronounced in thicker membranes with higher equivalent

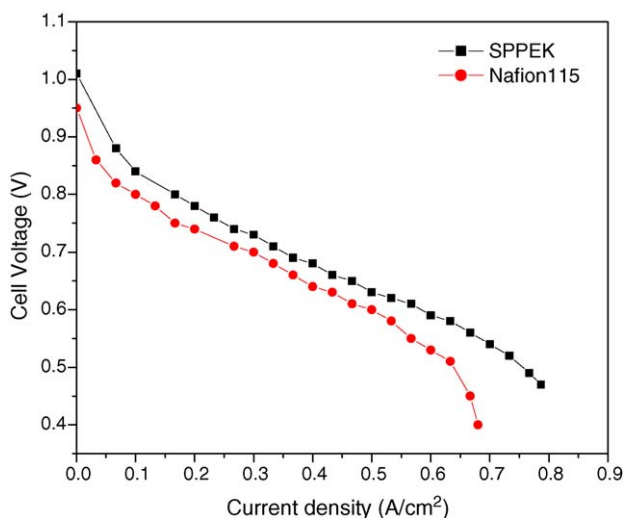


Fig. 2. Polarization curves of SPPEK PEMFC and Nafion 115 PEMFC.

weights (Nafion 115, EW 1100, dry thickness 125 μm) than that in thinner membranes with lower equivalent weights (SPPEK membrane, EW490, thick 80 μm). The equivalent weight and thickness influence much on the relevant properties of the membrane as PEM in the single cell, especially on the hydraulic permeability and water diffusivity through the membrane, which govern the back flow of water from the cathode side to replenish the water dragged away from the anode side. Presumably, the superior cell performance of the SPPEK PEM was resulted from these property characteristics.

The electrochemical impedance spectra (EIS) for the single fuel cells with SPPEK and Nafion 115 as PEM at 0.8 and 0.5 V are shown in Fig. 3. The semicircle nature in each spectrum could be fitted by the parallel combination of a resistor and a capacitor in the equivalent circuit, in series with a second resistor as shown in Fig. 4.  $R_1$ ,  $R_{ct}$  and  $C_{dl}$  are the bulk resistance, the charge-transfer resistance and the double layer capacitance, respectively.  $R_1$  could be obtained from the intersection of the semicircle with the real axis at higher frequencies (the first intersection), which represented the sum of the ionic contribution of the electrolyte membrane and the electronic contribution of the electrode itself. Usually  $R_1$  is attributed to the ionic resistance

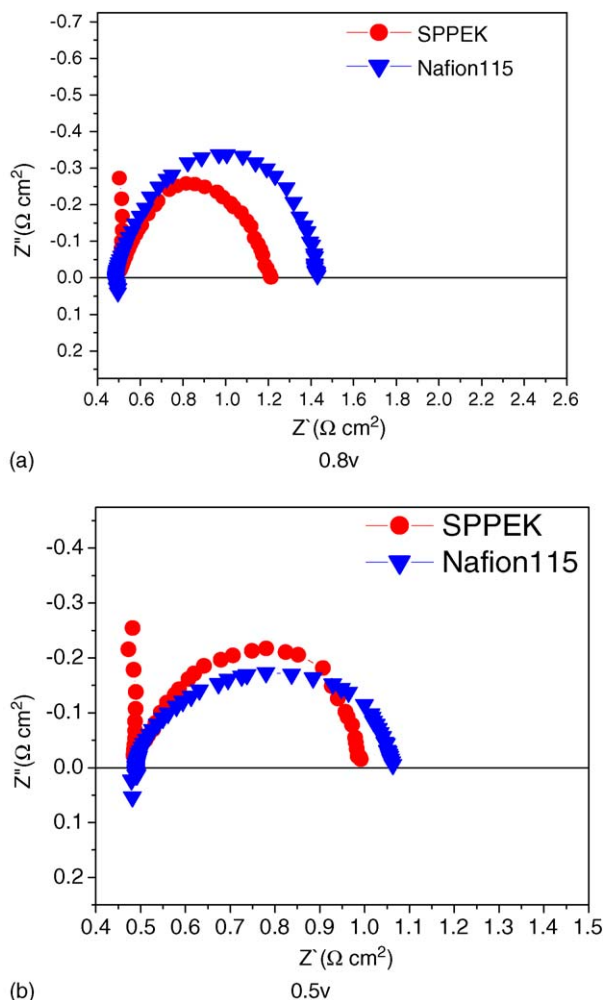


Fig. 3. Electrochemical impedance spectra of SPPEK PEMFC and Nafion 115 PEMFC.

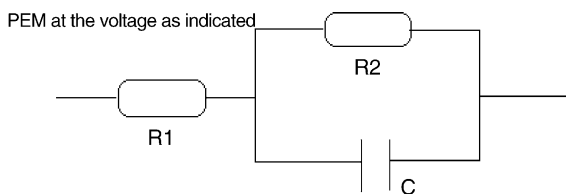


Fig. 4. Fitting circuit of electrochemical impedance of PEMFC.

of electrolyte in view point of the negligible electronic contribution of the electrode [30]. As shown in Fig. 3, the  $R_1$  of SPPEK and Nafion 115 PEMs was almost the same at both potentials of 0.8 and 0.5 V. This means that these two kinds of membranes had the same ionic resistance. The proton conductivity of SPPEK membrane is 0.44 times lower than Nafion 115 membrane, therefore, the SPPEK membrane with a thickness of 80  $\mu\text{m}$  should be used to function as Nafion 115 with a thickness of 125  $\mu\text{m}$  as reported in Table 1. Unlike  $R_1$ ,  $R_{ct}$  was influenced greatly by the operation conditions of PEMFC. As shown in Fig. 3, with the decrease of the potential, the diameter of the semicircle ( $R_{ct}$ ) decreased due to the increase of some driving force. By comparing SPPEK and Nafion 115 membranes as a PEM, the smaller diameter of EIS for the cell with SPPEK membrane indicated the lower charge transfer resistance and superior electrochemical performance. The experimental result also coincided with the polarization curves shown as in Fig. 2.

#### 4. Conclusions

The SPPEK membrane synthesized by the direct polymerization of sulfonated difluorobenzophenone and the bisphthalazinone monomer showed good thermal stability, high water affinity and reasonable proton conductivity. The PEM can be readily prepared using the as-made SPPEK membrane. The electrochemical performance of the single fuel cell was evaluated by polarization curves and electrochemical impedance methods. The experimental results demonstrated that under the conditions in this work, the PEMFC using SPPEK membrane as PEM showed superior cell performance compared to Nafion 115. Therefore, it appears to be very promising fuel cell membrane to substitute the commercial available perfluorinated membranes.

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